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SHOCK EMPLACED ARGON IN A STONY METEORITE.

Part I: Shock experiment and petrology of sample PART 2;

by

KURT FREDRIKSSON and PAUL DE CARLI (Stanford Res. Inst.)

Part II: A comparison with natural argon in its diffusion

by

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Shock Emplaced Argon in a Stony Meteorite

Part I: Shock experiment and petrology of sample

by

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Abstract

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A sample of the Bjurböle chondrite was exposed to artificial shock in an argon atmosphere. The sample consisted of grayish-white powdery material with chondrules. This shock changed the material to fine-grained black and well-indurated rock, similar to a black chondrite. Subsequent analysis (See Part II of this paper) showed that the shocked sample had incorporated considerable amounts of argon, most of which was retained even at high temperatures and was not released until the material was melted. These results support earlier suggestions that the irregular distribution of rare gases, as well as the light-dark structures in such meteorites as Pantar and Kapoeta, could have been caused by shock waves.

AUTHOR

Introduction

Shock waves presumably due to hypervelocity collisions between meteoritic bodies have recently been discussed by several authors. Fredriksson et al. (1962) ascribe the formation of the black veins present in many chondrites and black chondrites to such processes. Milton and

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DeCarli (1963) shock-loaded basalt, and their results indicate that shergotite (and maskelynite in general) is formed through the influence of shock waves. Fredriksson and Keil (1963) suggested that the light-dark structure as well as the distribution of rare gases in meteorites like Pantar and Kapoeta had been caused by shock processes. Lipshutz and Anders (1961) showed that diamonds in the Canyon Diablo iron meteorite probably had been formed by shock transformation. Fredriksson et al. (1962) also suggested that diamonds could be formed in stone meteorites in a similar fashion. It seems well established that shock events have been responsible for many features observed in meteorites, and hypervelocity impacts may also have been of importance in the formation of chondrules (Urey, 1952; Fredriksson, 1963).

The presence of primordial rare gases in exclusively the dark, presumably shock-induced, parts of some meteorites (e.g. Hintenberger et al., 1962; König et al, 1961; Signer and Suess, 1963), has been tentatively explained as selective trapping of these gases in minerals which underwent a phase transformation or melting during the shock processes (Fredriksson and Keil, 1963). The experiment reported below was conducted in order to test this possibility.

Details of the Experiment

Fragments, separate chondrules, and fine-grained matrix, of the Björböle chondrite (Ramsay and Borgström, 1902) were packed into a flat-bottomed stainless steel cylinder, 1" O.D. x 1/2 I.D. x 1/2" bottom thickness. The cylinder was evacuated to a pressure of ~500μ, then argon was admitted at 1 atmosphere. An aluminum seal ring and a stainless steel piston

were placed in the cylinder, and the piston was loaded with 20,000 lb. (100,000 psi). Thus the final thickness of the specimen was about 1/4 inch, and it contained an estimated 5-10% pore space occupied by argon at approximately 1-2 atmospheres. The specimen container assembly (protected from spalling by momentum traps) was then impacted by a steel plate 0.060" thick which had been explosively accelerated to a velocity of ~ 4.5 km/sec. Precise pressure calculations would require the Hugoniot equation of state for the compacted Bjurböle material. Furthermore, a thinner sample would be required in order to minimize the effects of shock reflections at the lateral steel-sample interface. However, a reasonable calculation of the peak pressure can be made with the following assumptions:

1. The Hugoniot equation for the sample is similar to that of dunite.

2. The effect of only one shock reflection, that from the bottom sample-steel interface, is taken into consideration.

3. The effects of pressure attenuation in the sample are ignored.

A graphical evaluation, using the Hughes-McQueen equation of state for dunite (Hughes and McQueen, 1958), yielded a peak pressure of 600 kb $\pm$ 150 kb. This estimate is corroborated by a number of actual measurements of shock pressures in similar geometries. (Bernstein, SRI, personal communication).

The temperature during shock is roughly proportional to the compressibility of the material. Therefore, the temperature for each mineral phase and for the gas in the pores was estimated separately. The temperatures indicated below are approximate, partly because of uncertainty about the pressure, partly because no accurate thermodynamic data are yet available for minerals at high pressure. For the pyroxene and olivine, the results of

Hughes et al. (1958) were used; the temperature during shock was in the range 300° - 700°C and fell adiabatically by 50 - 100°C immediately after the shock. For the more compressible minerals, such as feldspars and troilite, the temperature during shock was in the range 600°C - 1800°C; it fell adiabatically by 100 - 400° immediately after the shock. For the argon gas, the temperature during shock was of the order of 10,000°. No satisfactory estimate of the temperature immediately after shock could be made, because the final volume of the gas was not ascertainable. Since the quantity of gas in the container was so extremely small, the total heat content of the gas during shock was regarded as negligible.

Shock-induced alteration in the sample

After the shock described above, the grayish-white powder with chondrules had changed into a dark gray, well indurated rock with black "fragment". The changes in mineralogy (olivine of ultra-fine grain, secondary troilite etc.) and in structure were much the same as have been described in detail by Fredriksson et al. (1962). However, it may be added that the shocked sample strongly resembles for example the meteorite Pantar (Fredriksson and Keil, 1963; Wlotzka, 1963) with regard to both the gray parts and also the "black fragments".

Figure 1 shows a thin section of the natural Bjurböle chondrite with a black vein and a "black fragment". It is obvious that the "fragment", which continues into a black vein through a chondrule, could not be an extraneous piece but rather must have formed in situ and probably by some shock transformation of the mineral constituents. Figure 2 shows a thin section of the shocked sample of Bjurböle (which had been a powder with loose chondrules) containing a "black fragment" consisting mainly of fine-grained olivine and numerous veins and drops of secondary troilite.

These samples cannot be described as "polymict breccias" because of the light-dark structures, although they are originally agglomerates.

Conclusions

The argon determination on the shocked sample yielded ~ 0.001 cc STP per gram (see Part II of this paper). This corresponds to roughly 5% of the argon present in the pore space of the compressed powder. Therefore it has been shown that noble gases can be introduced into meteoritic minerals undergoing shock transformation; this supports further the suggestion (Fredriksson and Keil, 1963) that the light-dark structure of meteorites such as Pantar and Kapoeta was induced by shock events. Recent results by Hintenberger, Vilcsek and Wänke (in preparation) seem to indicate that different minerals in Pantar not only contain various amounts of noble gases, but also that the isotope ratios vary. This would at present be difficult to explain by a single shock event nor could it be accounted for by any other simple one stage mechanism.

Acknowledgement

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FIGURE CAPTION

Figure 1: Thin section of natural sample of the Bjurböle chondrite. Ordinary light; length of section = 3 mm. At the upper left, a dark part, so called "black fragment" continuing into a vein through a chondrule.

Figure 2: Thin section of shocked, originally powdry material of the Bjurböle chondrite. Ordinary light; length of section = 3 mm. At the upper left a shock induced black, opaque area mainly consisting of ultra-fine grained olivine and secondary troilite. Large parts of the rest resembles the "black fragment" in Figure 1. Note that surviving chondrules are sharply visible in the comminuted matrix.

Shock Emplaced Argon in a Stone Meteorite

Part II: A comparison with natural argon in its diffusion

by

R. O. Pepin*, J. H. Reynolds* and G. Turner*

Experimental Methods

The argon evolved from shocked and unshocked specimens of the Bjurböle chondrite (see Part I of this paper) was examined for several heatings. The samples were heated for one hour at temperatures of approximately 600°C, 1000°C, and 1600°C. The final heating was sufficient to melt the meteorite.

The samples, each of approximately one gram, were wrapped in a few milligrams of aluminum foil and heated by radio-frequency induction in a previously outgassed molybdenum crucible, to which a previously outgassed lid was affixed. The temperatures were estimated by operating the RF generator at settings which had given those temperatures in previous runs under the same conditions, when measured with a W-W/Re thermocouple imbedded in the base of the molybdenum crucible. The temperatures are thought to be accurate to within +100°C and -25°C.

The gases released were collected on activated charcoal throughout the heating and purified afterwards by exposure to a titanium getter. Neon and helium were removed by pumping on the sample when adsorbed on charcoal at -196°C. Xenon and krypton were removed from the sample by adsorption on charcoal at -80°C. The isotopic composition and the amount of the argon was measured statically in an ultra-high vacuum mass

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spectrometer which was calibrated before and after the experiments with an atmospheric sample of known volume and isotopic composition.

RESULTS

The results of the argon analysis are displayed in Table 1, where there is set out, for each sample and each temperature, the amount of each argon isotope released and the isotopic ratios. The errors in the amounts released arise principally from day-to-day variations in the spectrometer sensitivity and are thought to be less than 20%. The errors in the isotopic ratios, which are quoted individually in the table, arise principally from statistical fluctuations in the measured ratios and vary according to the character of the sample.

DISCUSSION

(1) Argon Release in the Present Experiments. The argon evolved from the unshocked specimen can be compared with the results of Geiss and Hess [1958], who carried out somewhat similar analyses for the Bjurböle chondrite. The total amount of A^{40}, A^{38}, and A^{36} found by them was 6050, 1.22, and 4.62 in units of 10^{-8} ccSTP/g. We found 5770, 1.21, and 4.43 which are in reasonable agreement. The differences can probably be attributed in part to variations in the preheating of the samples. Geiss and Hess [1958] preheated their samples at 100°C for 15 to 30 hours; we exposed the samples to a somewhat higher temperature for a short period during glass blowing in assembly of the apparatus. The release pattern with temperature for the argon isotopes is somewhat different in this experiment from that reported by Geiss and Hess [1958].

~~This will be discussed more fully below.~~ It will be noted that the isotopic composition of the argon from the unshocked meteorite is substantially different from atmospheric argon.

Examining the results for the shocked specimen, we note that the argon released at all temperatures is considerably more abundant than for the unshocked specimen, that this argon has very nearly the isotopic composition of argon from the atmosphere, and that differences from atmospheric argon, when significant, are in the direction to be expected from dilution with a meteoritic gas. It is evident that atmospheric argon has been dissolved in the meteorite by the shock process.

It is possible from the data in Table 1 to compute values for the diffusion coefficient (actually D/a^2) for argon in the stone at 600°C and 1000°C. We assume that each isotope is originally uniformly dissolved in the spherical grains of radius a and that this gas diffuses out as a single component. Values of D/a^2 for A^{36} and A^{40} in the unshocked specimen and for A^{40} in the shocked specimen are listed in Table 2. It is possible to distinguish between A^{36} diffusion and A^{40} diffusion in the unshocked specimen because A^{36} is essentially all of "primordial" origin whereas A^{40} is essentially all of radiogenic origin and these components are distinct. In the shocked specimen we are dealing essentially with pure atmospheric argon so that no such distinction can be made.

The values of D/a^2 for the shocked component are intermediate between the two unshocked components at both temperatures. The quantity D/a^2 for the shocked component does not differ from either unshocked component by more than a factor of 8 at either temperature. To the

first approximation, then, the argon dissolved in the meteorite by shock diffuses about as readily as either of the argon components dissolved in the meteorite by natural processes.

(2) Argon Release from Bjurböle Chondrules. In order to interpret the diffusion coefficients above, we have also calculated diffusion coefficients for the release of argon from .59 - .86 mm sized chondrules from the Bjurböle meteorite, based on more detailed experiments which we had carried out previously on this material. In this experiment, argon release was examined at temperatures ranging, in 100°C steps, from 200° to 1600°C. In Bjurböle the matrix material is very similar in appearance to the chondrules, so that such a comparison may be useful. The total A^{40} released from these chondrules was 6010 ± 1000 $\times 10^{-8}$ ccSTP/g which is very close to the value reported above for the total meteorite. The release patterns for A^{36} and A^{40} are plotted in Fig. 1. Both release patterns show two distinct maxima (at above 550°C and at about 1250°C) suggesting that there may be more than one component undergoing diffusion in each case. Values of D/a^2--calculated from the smoothed release patterns and the assumption of single component diffusion--are plotted in Fig. 2 and Fig. 3 for A^{36} and A^{40} respectively.

It is clear from both the release patterns and from the nature of the curves of D/a^2 vs 1000/T that it is a considerable oversimplification to assume single component diffusion with a fixed activation energy. In this case the release patterns would have a single maximum and the plots of log D/a^2 vs 1000/T would be straight lines. It is interesting to note that the complex curves for D/a^2 can be resolved into much more regular curves if two independently diffusing components are assumed.

Basically the low temperature maximum in the release curves is attributed to one component; the high temperature maximum, to another. The gas released in the temperature range corresponding to the bottom of the valley between the two maxima is then distributed between the two components by a numerical calculation based on diffusion coefficients calculated from the other temperature data and extrapolated into that region. The two diffusion curves so evaluated are also plotted in Figs. 2 and 3. For both isotopes the component released at high temperature is fitted by a straight line plot of log D/a^2 vs 1000/T, with a slope corresponding to an activation energy of about 70 kcal per mole. For both isotopes the low temperature component is fitted by a regular curve, ~~exhibiting some curvature~~. The curvature is in the direction to be understood as a result of prior argon leakage from the chondrules. This curvature is more pronounced in the case of A^{40} where unambiguous data were obtained down to 300°C.

Evernden et al. [1960] have observed similarly complex log D/a^2 vs 1000/T curves for diffusion of radiogenic A^{40} from Ontario microcline. These authors adopt a very different interpretation for the complexity in that case, pointing out that lattice rearrangements of the microcline can be expected to take place in the temperature region where the curve shows irregular behavior. It is perhaps less likely to expect lattice changes near 700°C in the high temperature minerals characteristic of the Bjurböle chondrite [Wood, 1962] but this possibility cannot be excluded.

The complexity found for the release of argon in the Bjurböle chondrules indicates that it is useless to attempt to calculate an

activation energy for release of the shock-emplaced component from the sparse data obtained on that specimen, although as stated above this gas is retained about as tenaciously as naturally emplaced argon. The D/a^2 values are plotted in Fig. 2 and Fig. 3 for the purposes of rough comparison.

(3) The Temperatures of Stone Meteorites in Space. The diffusion properties of A^{40} in stone meteorites at low temperatures are of importance in setting an upper limit to the temperature in space of stone meteorites. Goles, Fish and Anders [1960] point out that D/a^2 cannot have exceeded 5×10^{-20} sec^{-1} over the last 4×10^9 years in those stone meteorites which appear to have valid potassium-argon ages--i.e., ages in approximate agreement with the value 4.6×10^9 years, based on the Pb-Pb method for meteorites. These authors have extrapolated diffusion coefficients calculated from very limited heating experiments on various meteorites, namely Holbrook, Bjurböle, Richardton and Norton County [Geiss and Hess, 1958], to conclude that the temperature of the stones has not exceeded $196 \pm 30^{\circ}K$. It has always been appreciated that the extrapolation involved is to a range of diffusion coefficients vastly removed from the experimental data. It has perhaps not been sufficiently appreciated how uncertain the diffusion coefficient is in the experimental region: the present detailed data for Bjurböle chondrules show that the curve to be extrapolated is not a straight line.

An extrapolation, using Fig. 3 of the low temperature A^{40} component would place an extreme upper limit on the space temperature of the meteorite of $320^{\circ}K$. But the possibility exists of the temperature limit being considerably lower than this. If, for example, the meteorite had

already lost 8% of its argon before our experiment was performed, the slope of the low temperature log D/a^2 vs 1000/T plot would be reduced from 40 kcals/mole to 20 kcals/mole and the temperature limit reduced to 220°K. Such a loss is quite consistent with the measured K-A age [Geiss and Hess, 1958].

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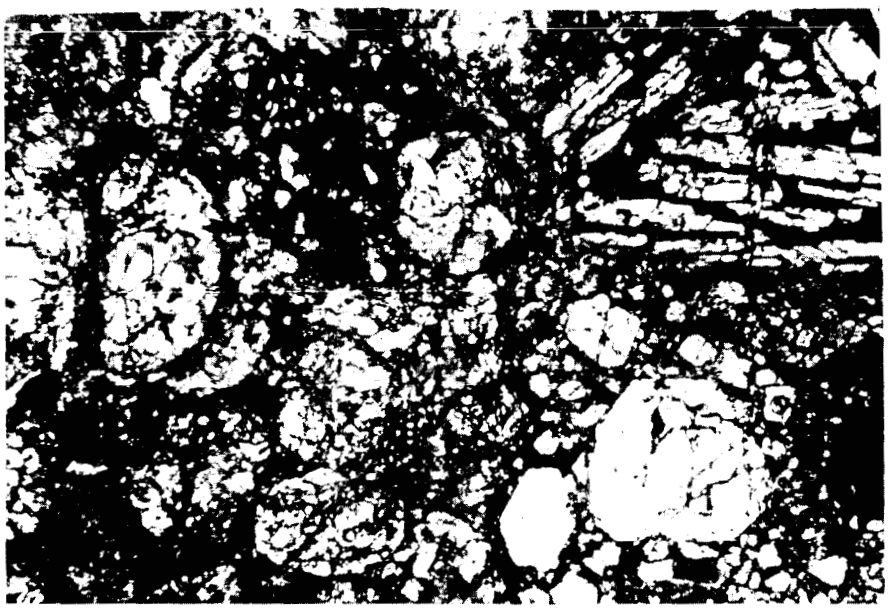

FIGURE 1

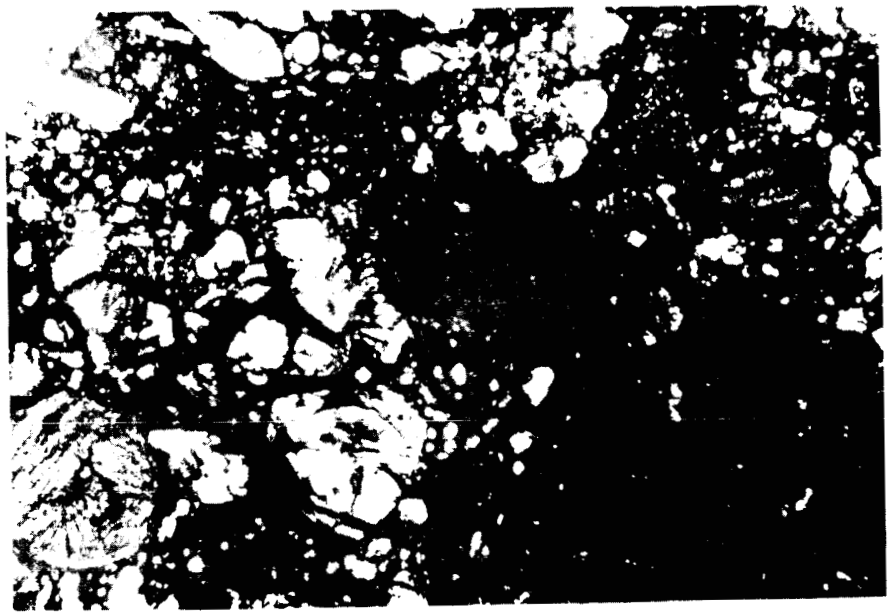

FIGURE 2

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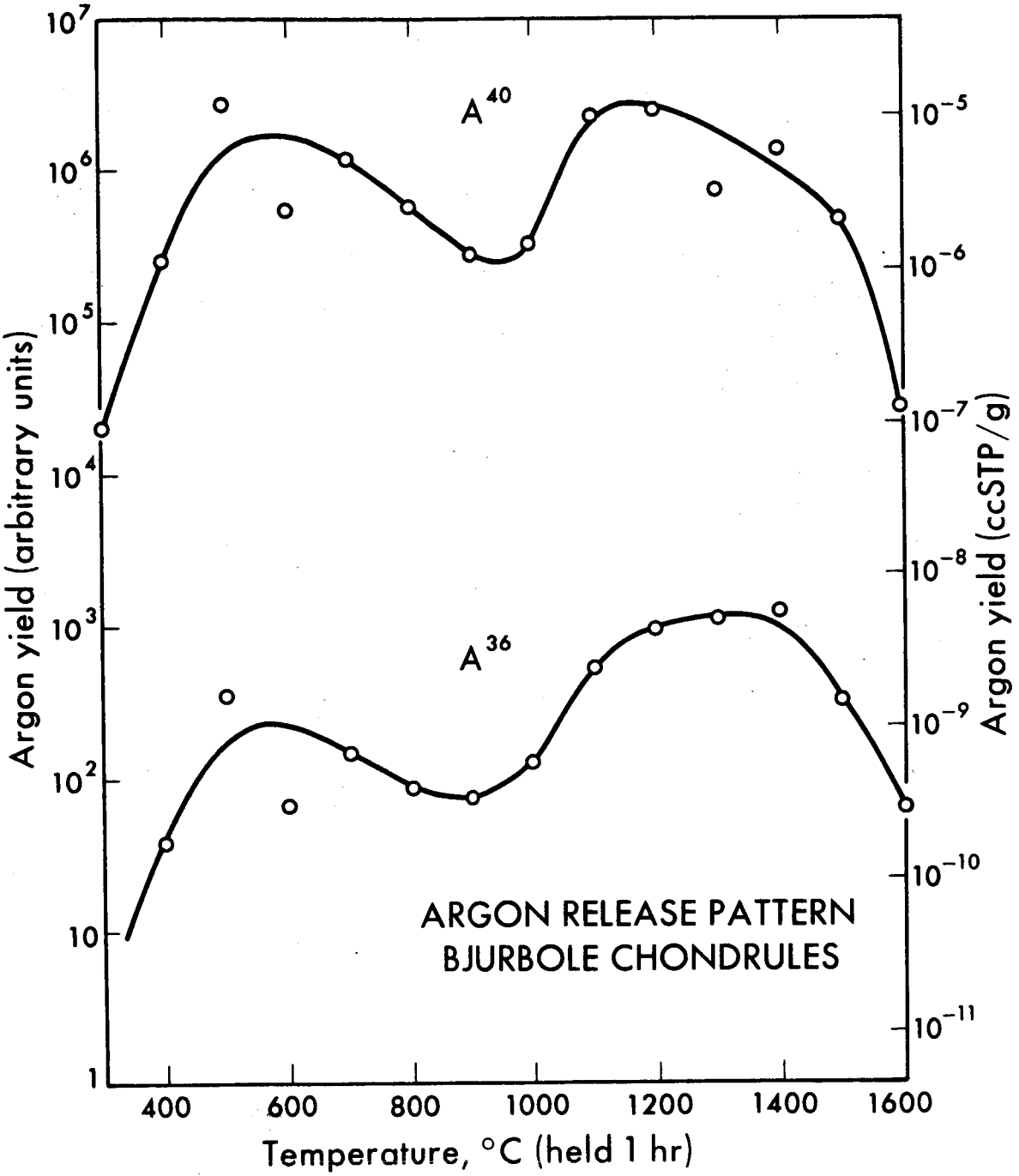
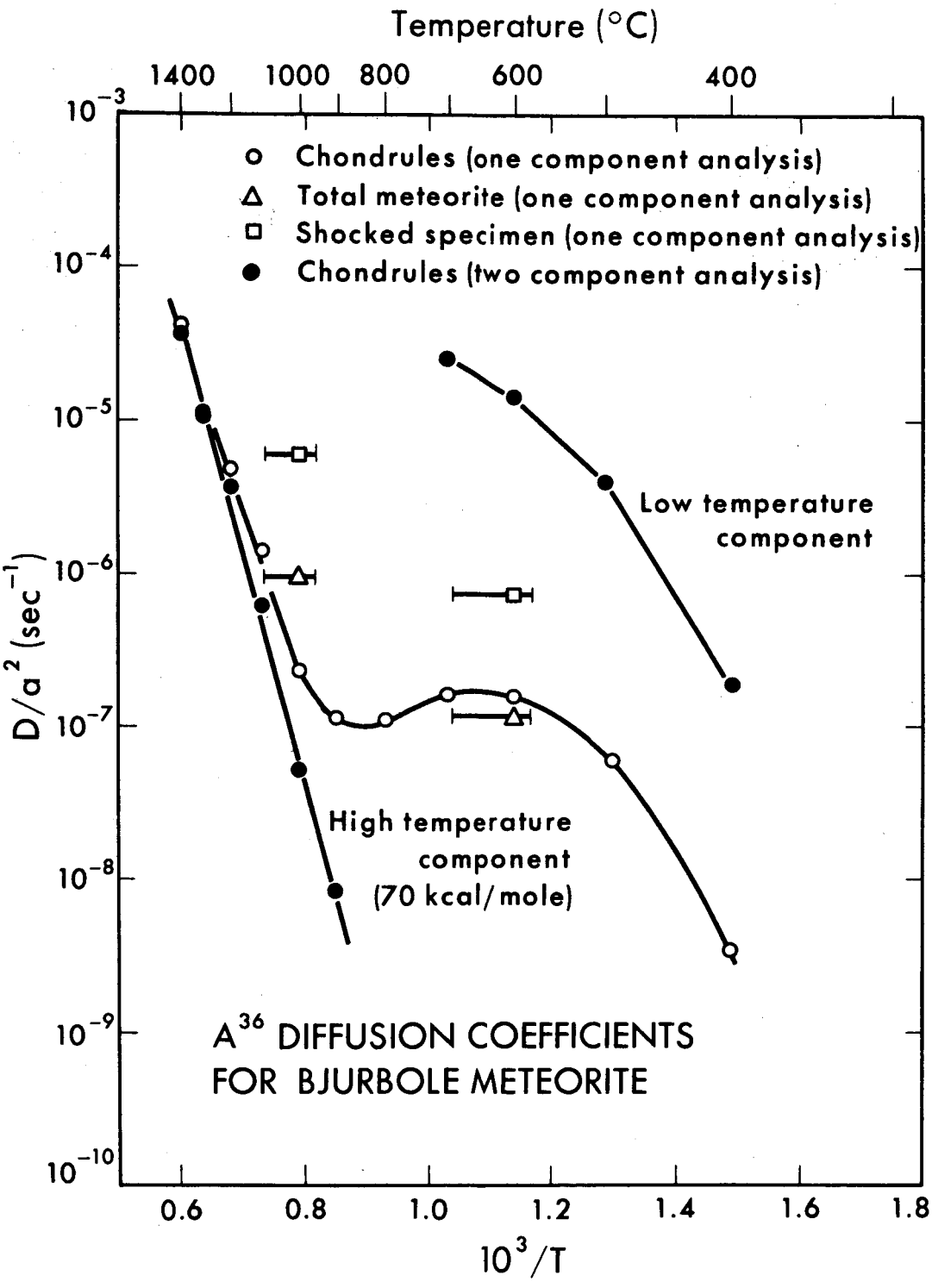
TABLE 1. Argon Yields (per gram)

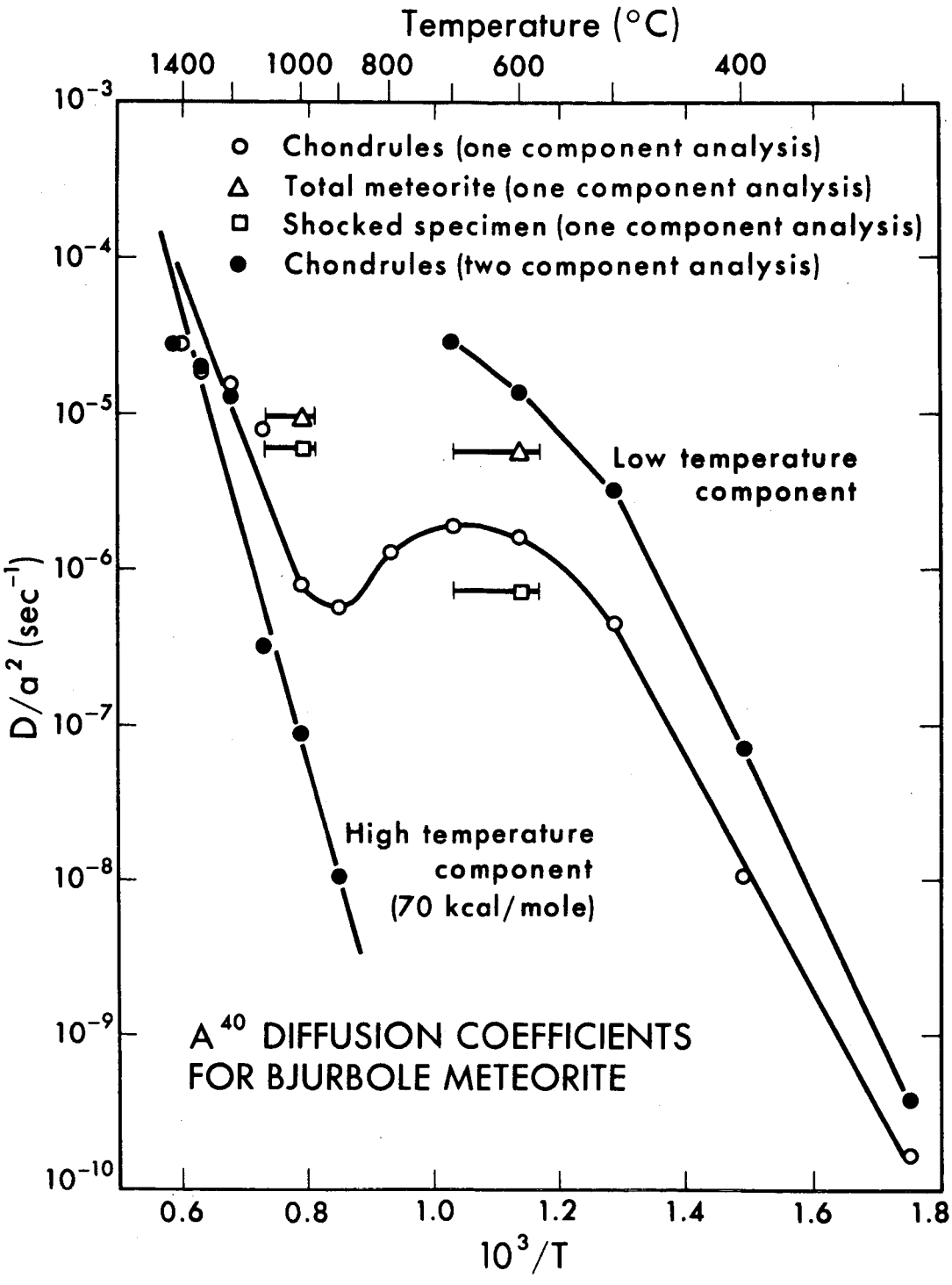
Temperature	A^{36} $\times 10^{-8}$ ccSTP	A^{38} $\times 10^{-8}$ ccSTP	A^{40} $\times 10^{-8}$ ccSTP	$\frac{A^{40}}{A^{36}}$	$\frac{A^{36}}{A^{38}}$
Unshocked					
~ 600°C	0.29	0.082	2440	8280 ± 400	3.59 ± .40
~ 1000°C	0.47	0.16	1170	2510 ± 60	2.93 ± .09
~ 1600°C	3.67	0.97	2160	588 ± 3	3.77 ± .03
TOTAL	4.43	1.21	5770	1300	3.64
Shocked					
~ 600°C	55.0	10.1	16700	304 ± 1	5.43 ± .07
~ 1000°C	110.	20.3	32700	298 ± 1	5.40 ± .04
~ 1600°C	196.	38.0	59300	302 ± 1	5.15 ± .04
TOTAL	361	68.4	108700	301	5.27
Air				296	5.35

TABLE 2. Diffusion Coefficients

Temperature	Diffusion coefficients (D/a^2) sec^{-1}		
	Unshocked, 36	Unshocked, 40	Shocked, 40
~ 600°C	1.18×10^{-7}	56.5×10^{-7}	7.27×10^{-7}
~ 1000°C	9.5×10^{-7}	95×10^{-7}	60.0×10^{-7}


10^7
10^6
10^5
10^4
10^3
10^2
10
1
A^{40}
A^{36}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
Argon yield (arbitrary units)
Argon yield (ccSTP/g)
ARGON RELEASE PATTERN
BJURBOLE CHONDRULES
400
600
800
1000
1200
1400
1600
Temperature, °C (held 1 hr)


Temperature (°C)
1400
1000
800
600
400
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
D/a^2 (sec^{-1})
Chondrules (one component analysis)
Total meteorite (one component analysis)
Shocked specimen (one component analysis)
Chondrules (two component analysis)
Low temperature component
High temperature component (70 kcal/mole)
A^{36} DIFFUSION COEFFICIENTS FOR BJURBOLE METEORITE
0.6
0.8
1.0
1.2
1.4
1.6
1.8
$10^3/T$


Temperature (°C)
1400
1000
800
600
400
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
D/a^2 (sec^{-1})
Chondrules (one component analysis)
Total meteorite (one component analysis)
Shocked specimen (one component analysis)
Chondrules (two component analysis)
Low temperature component
High temperature component (70 kcal/mole)
A^{40} DIFFUSION COEFFICIENTS FOR BJURBOLE METEORITE
0.6
0.8
1.0
1.2
1.4
1.6
1.8
$10^3/T$